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Technical Report

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Office of Naval Research

on

The Electrochemical Polarization of Zirconium in NaCl Solutions

by

Norman Hackerman and Olin B. Cecil

1 December 1952

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Department of Chemistry  
The University of Texas  
Austin, Texas

## Electrochemical Polarization of Zirconium in NaCl Solution

by

Norman Hackerman and Olin B. Cecil

### Summary

Cathodic and anodic polarization curves of zirconium in neutral sodium chloride solution were determined at constant current densities in the range of  $3.5 \times 10^{-8}$  to  $3.5 \times 10^{-3}$  amp./cm.<sup>2</sup>. All potentials were steady-state potentials.

In aerated 0.5 molar NaCl, the cathode reaction occurring below the oxygen limiting diffusion current of  $2 \times 10^{-4}$  amp./cm.<sup>2</sup> was the reduction of O<sub>2</sub> to OH<sup>-</sup>. At current densities above the diffusion wave, hydrogen was evolved. A change in salt concentration resulted in a slight shift of the diffusion current due to different oxygen solubilities in the different salt concentrations. In de-aerated 0.5 molar chloride solution, the oxygen diffusion current decreased with a decrease in oxygen concentration. The value for the slope of the Tafel line was 0.12, and the hydrogen overvoltage was 0.83 volt at 1 milliamp./cm.<sup>2</sup>.

Another wave occurred at  $2 \times 10^{-6}$  amp./cm.<sup>2</sup> and can best be explained as the reduction of a surface oxide layer on the metal.

Anodically, zirconium dissolved in 0.5 molar NaCl. The dissolution potential, 0.15 volt, was constant with a change in current density. Commercial zirconium and pure hafnium also dissolved under similar conditions.

In neutral sulfate solutions, zirconium was passive under anodic treatment. At the higher current densities, above  $1 \times 10^{-3}$  amp./cm.<sup>2</sup>, the potential apparently reached a constant value in about ten minutes followed by a sudden increase in potential to 28.5 volts. This high potential was a result of an IR drop across a surface layer of oxide present on the zirconium coupon.

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### Introduction

Other than in the last few years, only sporadic investigations on the electrochemical behavior of zirconium have appeared in the literature. In 1831, Becquerel (1) reported the electrodeposition of black, amorphous zirconium metal from aqueous chloride solutions. After that, little attention was paid to the problem of electrodeposition of the metal until Bradt and Linford (2) confirmed Becquerel's findings and extended the study of the problem.

A similar lack of information exists concerning one of the most unusual properties of the metal--the anodic valve action. It was recognized as early as 1913 that, under anodic conditions, the metal would act as an electrolytic rectifier (3). Supposedly, this rectification is brought about by the action of a passivating layer of  $ZrO_2$  formed during the anodic treatment. The effect is principally observed in sulfuric acid, chromate and dichromate solutions. Warner and his co-workers (4) have shown that the presence of salts, such as fluoride, destroys this passive layer of the oxide. No work has been reported, though, on the action of these latter salts alone.

Cathodic polarization curves obtained by Warner have all been in the current density range of  $2 \times 10^{-4}$  amp./cm.<sup>2</sup> and higher. In this region, hydrogen is being evolved at the zirconium cathode. As yet, no investigations have been reported on the action on zirconium of anodic or cathodic treatment in a low current density region (ca.  $10^{-5}$  amp./cm.<sup>2</sup>).

The corrosion characteristics as obtained from the metal under common conditions have been well established of late. More corrosion resistant than titanium, zirconium is resistant to all concentrations of hydrochloric, nitric and phosphoric acids; but is attacked by wet chlorine and by concentrated sulfuric acid.

### Scope of this Work

In this investigation, cathodic and anodic polarization curves were established over the current density range of  $10^{-3}$  amp./cm.<sup>2</sup> to  $10^{-8}$  amp./cm.<sup>2</sup>. Sodium chloride solutions were chosen because of their highly corrosive action on most metals. Work in neutral sulfate solutions was performed to compare the anodic action of zirconium and titanium. The effect of oxygen concentration was also examined.

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### Experimental

#### Materials

All of the metal samples used in this work were supplied by the Argonne National Laboratories. Hafnium-free zirconium was about 98.6% pure; oxygen accounting for 1.34%, the remainder mostly carbon. The metal was furnished in the form of punched coupons 3/4 inch in diameter and 1/10 inch thick. Commercial zirconium and the pure hafnium samples were machined coupons of the same dimensions.

Reagent grade sodium chloride was used in preparing the chloride solutions employed. The correct amount of salt was weighed out in a container and dissolved in sufficient distilled water to give 5.0 liters of solution of the desired concentration. Any evaporation losses during the run were replaced with distilled water to keep the correct concentration. The sulfate solutions were prepared in an analogous manner with reagent grade, anhydrous sodium sulfate. No attempt was made to buffer the solutions, keeping them as simple as possible.

It has been observed in previous work in this laboratory (5) that iron, present in the sodium chloride solutions as an impurity, was precipitated as the hydroxide during the course of a run. Although this offered no obstacle for cathodic studies, the precipitate would migrate to the zirconium electrode under anodic treatment. This could not be tolerated, and steps were taken to remove the iron present.

One method used was aeration and subsequent filtration of the electrolyte solutions. The correct amount of the salt was prepared as a nearly saturated solution, aerated for 12 to 18 hours, filtered through a fritted glass crucible, and diluted to volume.

Although solutions prepared in this manner showed no signs of a precipitate during the runs, the question arose as to the possible presence of other interfering ions. To examine this possibility, the solutions were pre-electrolyzed for 12 to 24 hours with carbon electrodes. Only the pre-electrolyzed solutions were used in the air-free runs.

The air-free solutions were pre-electrolyzed, as just discussed, and filtered. After filtration, the solutions were boiled to expel all dissolved gases. While at the boiling temperature, the

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container was closed with a stopper containing two glass tubes; one reaching to the bottom of the flask, and the other extending just below the stopper. On stoppering the container, purified nitrogen was passed through the solution until the electrolyte had reached room temperature. The two tubes were then closed off by stopcocks until the solution was used.

#### Coupon Casting

Successful castings were obtained with a pressure molding process employing a colorless, transparent, lucite extrusion powder furnished by the E. I. Du Pont De Nemours and Company. The casting procedure was quite simple and all of the coupons that were cast were usable. No apparent aging or cracking was observed after as much as 300 hours' use.

The mold used for these castings was a steel cylinder, having an inside diameter at the bottom of 1 1/2 inches and a depth of 2 1/2 inches, mounted on a 1/4 inch steel base. A 2° inside taper allowed easy removal of the molded specimens. A solid steel cylinder 2 inches long and 1 1/2 inches in diameter functioned as a piston. Pressure was applied by means of a screw acting on the piston. A 15 turn coil of 0.030 inch nichrome wire served as the heating element.

For molding, the metal specimen was placed on the bottom of the mold and the lucite powder was added to a depth of about 1 1/2 inches. The steel piston was inserted and pressure applied with the screw until hand operation of the screw could cause no further movement of the piston. The mold was then heated. Twenty volts A.C. across the heating coil was quite sufficient for the necessary temperature. At this voltage, the coil drew 4 amperes current. The pressure was checked periodically and was maintained as previously described. When the inside temperature became high enough to cause the lucite to become plastic, hand pressure on the screw could cause a large movement of the piston. After this single sudden change, no further pressure increase could be obtained on increased heating. The heater was then disconnected and the mold allowed to cool. On cooling, the lucite contracted. If the piston was again forced in, on reheating, the expansion of the lucite exerted a large pressure. Several cycles of this procedure gave a clear mold which was easily removed.

After being removed from the mold, the coupon was faced down and machined to the proper size on a lathe. A 1/4 inch hole

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was drilled through the plastic to the back surface of the metal to allow means for making electrical contact to the coupon. The coupon was then polished on No. 2 metallographic emery paper until a flat surface was obtained.

#### Aerated Apparatus

All aerated investigations were performed in apparatus described in detail elsewhere (5), only a brief description will be given here. The multicelled apparatus enabled the operation of six cells simultaneously. The only requirements were that all cells be run either anodically or cathodically and near enough in the same current density range to operate from the same supply voltage.

The electrode assembly of each cell consisted of the metal electrode under investigation, an auxiliary polarizing electrode, and a reference electrode. The metal coupon serving as an electrode was mounted in a laminated phenolic plastic holder. Electrical contact was made to the back of the metal by means of a copper lug held in position by a brass spring. The back was sealed with a threaded cap of the same phenolic plastic.

The auxiliary polarizing electrode was made by sealing a platinum wire through the end of a soda-glass tube. Six turns of the wire around the end of the glass tube actually served as the electrode. External electrical contact was made by means of a length of copper wire welded to the platinum and running through the center of the glass tube.

A saturated calomel electrode with a side arm filled with a 2% saturated KCl-agar gel served as the reference electrode.

The three electrodes were mounted in one holder such that the platinum electrode was 7 cm. from the coupon face; the reference half cell was situated so that the side arm could be adjusted at different distances from the coupon surface. This adjustment made it possible to determine, and correct for, the IR drop of the solution between the coupon and the reference cell. This will be discussed more in detail later. The assembly holder was supported from a beam which was connected to the circular stirring mechanism; enabling all three electrodes to maintain the same relationship with each other at all times.

The solutions in the cells were kept saturated with air by means of a fritted glass gas dispenser, fitted with a glass chimney

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reaching nearly to the surface of the solution. The air passing through the dispensers had been previously washed and humidified by bubbling through a distilled water column packed with small pieces of glass tubing. Any oil present in the air was removed by a cotton filter placed in the compressed air line.

#### Air-Free Apparatus

A similar apparatus was constructed for the studies involving the effect of oxygen concentration. The stirring mechanism was identical with that used in the aerated apparatus, except that it was constructed on a smaller scale. Because of space limitations, only the coupon being studied was rotated. The speed of rotation was 32 rpm. The multiple cell arrangement was maintained so that a complete polarization curve could be obtained without depletion of the vanadyl sulfate solutions used to remove oxygen from the tank nitrogen. Six plastic cells, 4 x 2 inches and 4 inches deep were used. A cover fitting over each container held a platinum auxiliary polarizing electrode, a calomel reference electrode, and a tube used to fill the cells with electrolyte.

The component parts of the assembly were contained in a wooden box 31 1/2 x 13 1/2 inches and 13 inches high. The top was sealed with a rubber gasket and held in place by six bolts. The entire inside surface was coated with white Ucilon lacquer. The stirring mechanism was activated by means of a pulley-belt arrangement on a shaft extending through the box. The opening around the shaft was packed with grease to give an air tight fit.

Air was removed by flushing the box with purified nitrogen for a long period of time. Oxygen was removed from the nitrogen with a vanadyl sulfate solution according to the method of Meites and Meites (6).

De-gassed solutions were forced into the cells, through stopcocks passing through the side of the box, with nitrogen pressure. Electrical contact was made from the cells to terminals with connections on both the inside and outside of the box.

A cut-away view of the apparatus is given in Figure 1, showing one cell arranged for operation. The platinum auxiliary polarizing electrode was fitted with a glass case closed at the bottom with a fritted glass disk and with an exit to the outside atmosphere at the top. With this arrangement, any gas evolved

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at this electrode during a run was allowed to escape to the atmosphere rather than enter the solution.

The zirconium coupons used in the air-free runs were mounted quite differently from those used in the aerated runs. Since available space was a limiting factor, no plastic molding of the coupons could be used. Therefore, the problem was of a suitable masking of the coupon to give the desired area. The procedure finally selected employed sealing a thin lucite disk on the surface of the previously polished metal with clear Ucilon lacquer. The lucite disk had been previously punched with a paper punch and gave fairly reproducible areas. The Ucilon did not adhere firmly to the plastic and the disk could be removed when the lacquer had completely dried, leaving a good mask of Ucilon on the metal. The coupon was then placed in a brass holder and electrical connection made with a threaded contact set in the holder. Connection to the outside was made by a second contact at the other end of the holder. The coupon and holder were then coated with ceresin wax. It was observed that the wax would flow easily over the Ucilon base and leave, intact, the desired unmasked part of the metal surface.

The holder was thoroughly insulated with three layers of baked-on shellac. Where the holder passed through the metal attachment to the stirrer, a piece of small bore tygon tubing was used as additional insulation. No breakdown of the insulation was noted when tested with as much as 45 volts. The highest operating voltage used was 12 volts.

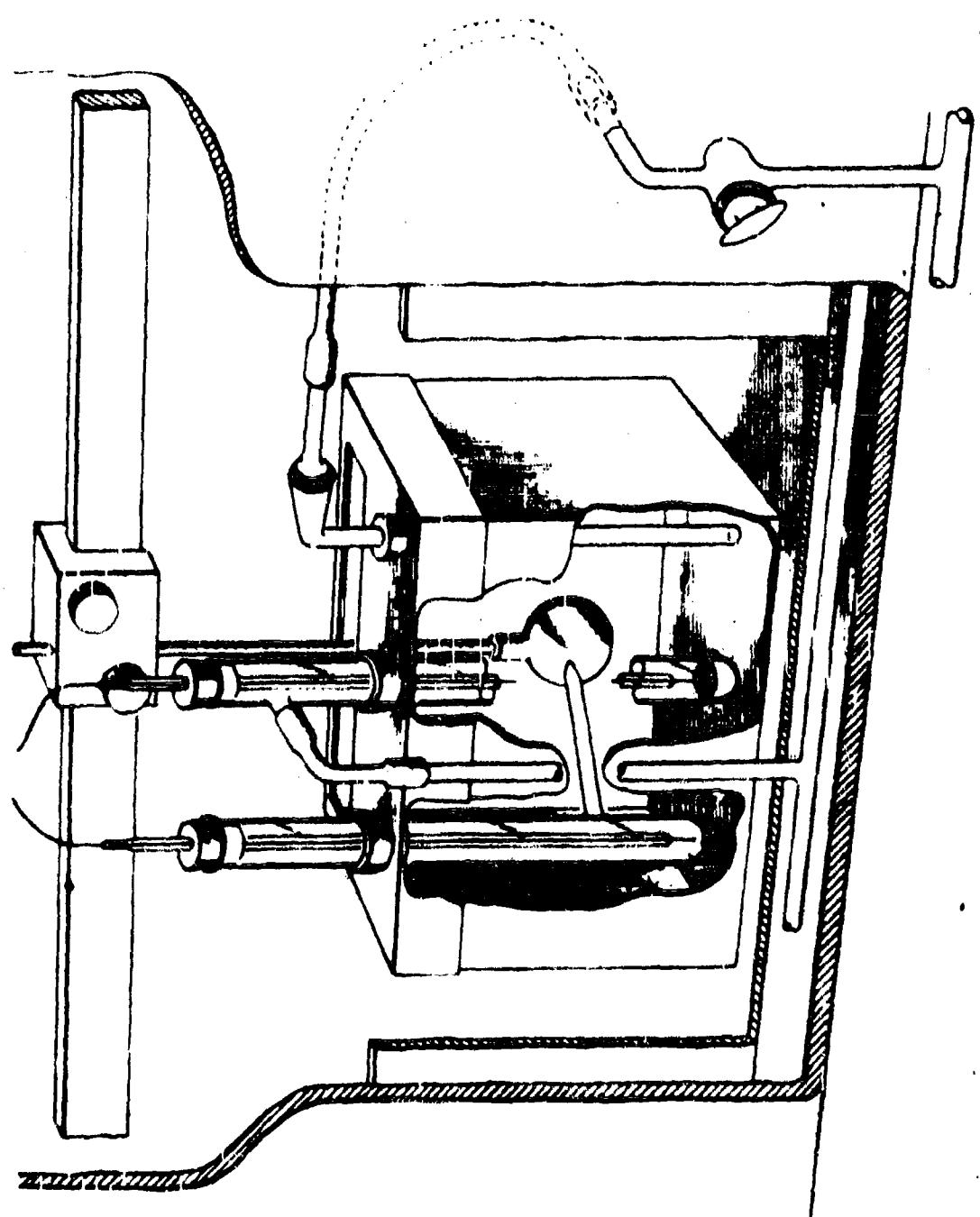
#### Measuring Circuits

The basic circuits used have been described elsewhere (5), so only a brief description will appear here. Since the polarization required a constant current, a supply voltage much higher than the potential across the cell was used. In this manner, most of the voltage drop was across external dropping resistors and any variation in current due to changes in potential across the cell was minimized. The supply voltage for currents below 1 ma. consisted of a bank of dry cells. Higher currents were obtained from storage batteries. The external dropping resistors consisted of several fixed and two variable resistors of which any series combination could be placed in the circuit. This enabled close adjustment of the current passing through the cell.

Current through the cell was set by connecting a potentiometer

**FIGURE 1**

**Cell for air-free measurements**



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across a wire-wound resistor of 1% tolerance, calibrated by a Wheatstone bridge to  $\pm 0.1\%$  or better, and properly adjusting the dropping resistors to give the previously determined IR drop across this standard resistor. For making potential readings, a system of knife-edge switches connected a thermionic amplifier in series with the potentiometer and both in series with the calomel reference electrode and the coupon being studied.

Since many of the polarizing currents were of the order of  $10^{-6}$  ampere, it was necessary to use a thermionic amplifier, which draws only  $10^{-12}$  to  $10^{-14}$  ampere, in conjunction with the conventional potentiometer. The amplifier consists, essentially, of a Wheatstone bridge circuit, one arm of which is the cathode to grid portion of a triode. The conduction of the tube depends on the bias potential on the plate of the tube. If the potentiometer and the cell potential are not the same, the potential of the plate becomes more or less negative, causing an unbalanced condition of the bridge. This, in turn, is reflected in the galvanometer and the potentiometer is adjusted to give a balanced condition.

The same measurement network was used for measurements on the air-free runs. The connections from the air-free apparatus to the circuit control board were made with a multiple conductor cable. No detectable current leakage between the various wires of the cable could be detected, even under an applied potential of 45 volts. Specific pieces of apparatus employed, all Leeds and Northrup instruments, were: a type K-2 potentiometer, a thermionic amplifier, Catalog Number 7673, and a galvanometer, Type R, List Number 2500e, with a sensitivity of 0.003 microampere per millimeter deflection and with a period of 3 seconds.

#### Measurements

Prior to beginning each run, the fritted glass gas dispensers were cleaned with concentrated hydrochloric acid followed by a thorough rinsing with distilled water. The platinum electrodes were cleaned in 1:1 nitric acid and rinsed with distilled water.

The coupons were polished by hand on metallographic emery paper, starting with No. 2 grade paper and finishing with No. 2/0 grade. The procedure was completed by cleansing with 95% ethyl alcohol and wiping with clean, dry lens tissue. In one study, a zirconium coupon was polished in the usual manner followed by etching in 2.5% aqueous hydrofluoric acid for 10 seconds, rinsing in 2 N sulfuric acid, and thorough washing with

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distilled water.

The various electrodes were assembled and placed in position. The solutions for the aerated runs had been previously placed in their cells in the thermostat and brought to the correct temperature. In the air-free runs, the solutions were transferred to their appropriate cells only after the apparatus had been thoroughly flushed with nitrogen. The method of transfer has already been discussed.

Since the same control board was used for measurements in both pieces of apparatus, the procedure hereafter discussed was applicable to both the aerated and air-free runs.

The dropping resistors were set at the approximate value for the necessary current. An approximate value for the dropping resistors could be calculated by allowing from 2 to 4 volts dropped across the cell. Although this was satisfactory for most cases, in some of the anodic studies much more than this drop was required. In adjusting the current through the cell, the potentiometer was set at the calculated value of IR drop across the standard resistor. When placed in the circuit, the potentiometer was balanced with the dropping resistors until the galvanometer gave a null indication. In most instances, this could be accomplished in less than one minute.

All potential measurements were made with the thermionic amplifier in the circuit. Often the variations in the potential were quite large and the average value obtained for several seconds was recorded as the potential. In none of these runs did the current vary enough to necessitate a separate potentiometer circuit for its control while potential readings were being made.

All potentials recorded as final potentials were steady state values. The criterion for steady state was a constant potential for a period of at least four hours. Although most points were obtained from separate coupons, it was found necessary and desirable in some cases to run the same coupon at several values of current density. To do this, it was necessary only to adjust the dropping resistors to give the new current density after a steady state had been reached for the previous point.

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### Results

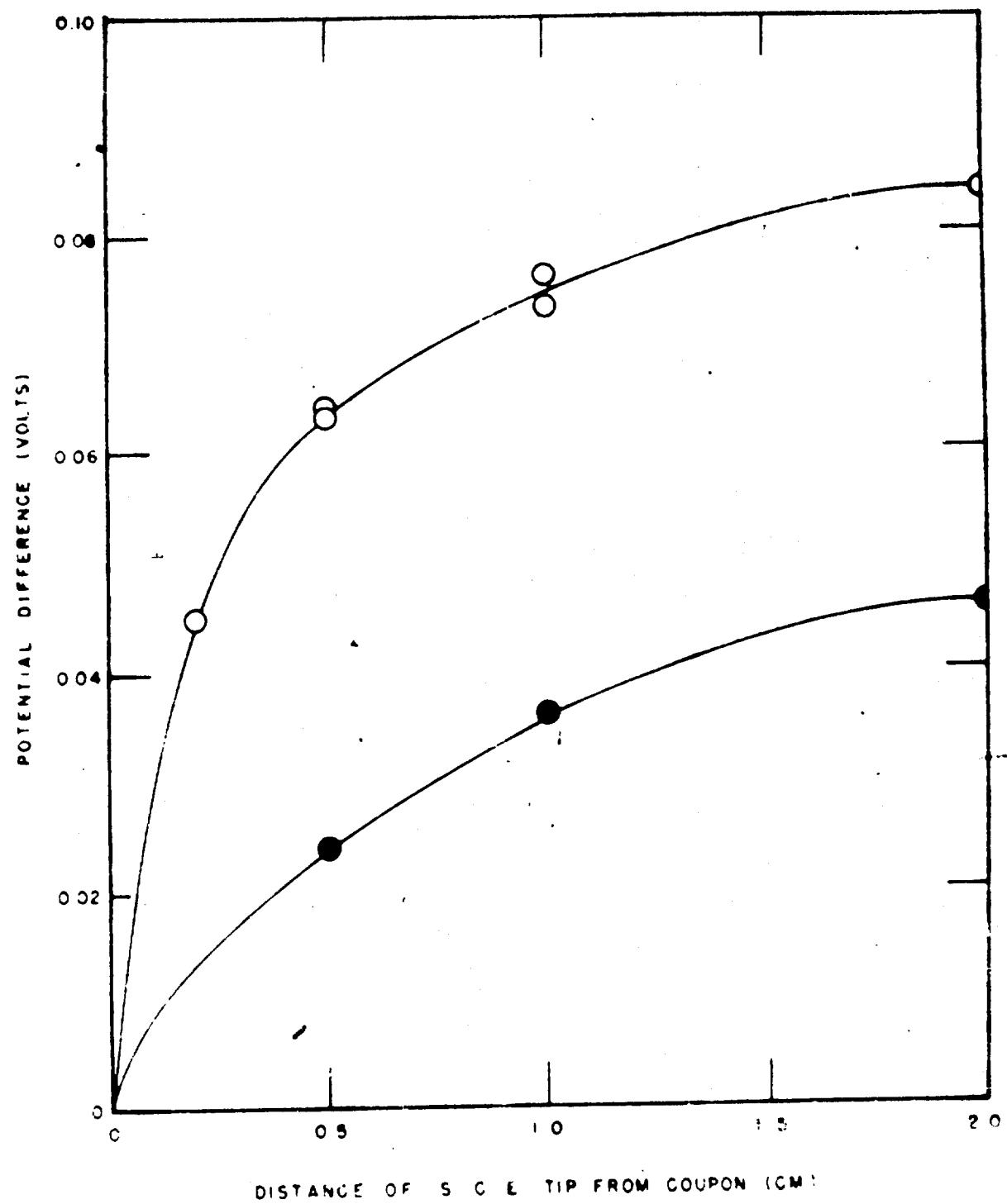
All of the measurements in the aerated investigations were made at  $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . Studies involving the effect of oxygen concentration were performed at room temperature; in this instance,  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The potentials were recorded with respect to the saturated calomel electrode. The European convention of polarity is followed throughout this work.

### Corrections for IR Drop in the Solution

It has been found (5) that if the potential measurements are made with the tip of the calomel electrode salt bridge against the coupon surface, the potential changes by several millivolts during a period of a minute or more after the tip was moved against the surface. This effect was attributed to blocking off the polarizing current from the portion of the coupon surface where the measurement was being made. All potentials were measured, therefore, 2.0 cm. distance from the coupon surface. The potentials were in error by the amount of the IR drop through the 2.0 cm of solution. The potential errors were negligible except in the higher portion of the current density range. In this range, corrections were made.

Because of the current distribution, a non-uniform potential gradient existed across the 2.0 cm. of solution, but the geometry of the system was not known well enough to enable a calculation of the solution resistance. To determine this resistance, two series of readings, each at a different current, were made of the potentials at different distances from the metal electrode in the 0.5 molar NaCl solution. The potentials were read as soon as the calomel electrode tip was moved to a different distance from the coupon surface. See Figure 2. The non-uniformity of the potential gradient of the solution, due to the spreading of current lines as they leave the surface, is reflected in the non-linearity of the curves. The resistance of the 2.0 cm. of solution used in calculating the corrections is the potential difference at 2.0 cm. from the surface divided by the current. For the 5 and 10 ma. curves, the values are 8.4 and 9.2 ohms respectively, the average value being 8.8 ohms. The value for the resistance for 1.0 molar NaCl, 6.6 ohms, was calculated using the ratio of the specific resistances of the two concentrations. The effect of the corrections is such as to decrease the apparent amount of polarization. Thus, the potential is less negative in cathodic polarization and less positive in anodic polarization.

**FIGURE 2**  
In 0.5 molar NaCl, 30°C,  
● 5 ma.  
○ 10 ma.



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#### Roughness Factor Measurement

Roughness factor of a metal is defined as the ratio of actual surface to the apparent or projected surface of the metal. The roughness factor of several zirconium coupons, polished in the usual manner, was determined by a small volume gas adsorption method using krypton gas as the adsorbate. The value obtained was  $2.6 \pm 0.4$ .

Unless otherwise stated, all values of current density given in this work are stated in terms of amperes per square centimeter or projected area, amp./cm.<sup>2</sup>.

#### pH of the Solutions

The pH of the unbuffered NaCl solutions was measured from time to time during aerated runs at various current densities with a Beckman pH meter. The solutions were left unbuffered so that any effects on the electrode potentials or on the surface of the coupons due to the additional constituents in the solution would not be encountered. Because of the nature of the apparatus used in the air-free studies, the pH of those solutions were measured only after the completion of the run. No polarizing current was passed through one of the solutions during the run, enabling the pH of that solution to serve as a comparison for the others. In all aerated runs and most of the solutions used in the air-free run, the pH was  $6.5 \pm 0.3$ . However, in the air-free solutions run at high currents for extended periods of time, the pH was as high as 8.0 at the completion of the run.

#### Effect of Pre-electrolysis of Solutions

The effect of pre-electrolysis of the solutions on the polarization potentials of zirconium was determined by running two coupons at the same current density; one in a pre-electrolyzed salt solution and the other in a salt solution prepared by aeration and filtration in the usual manner. Several such determinations were made, anodically, cathodically, and at different current densities. No difference in potential was noted in any of the runs.

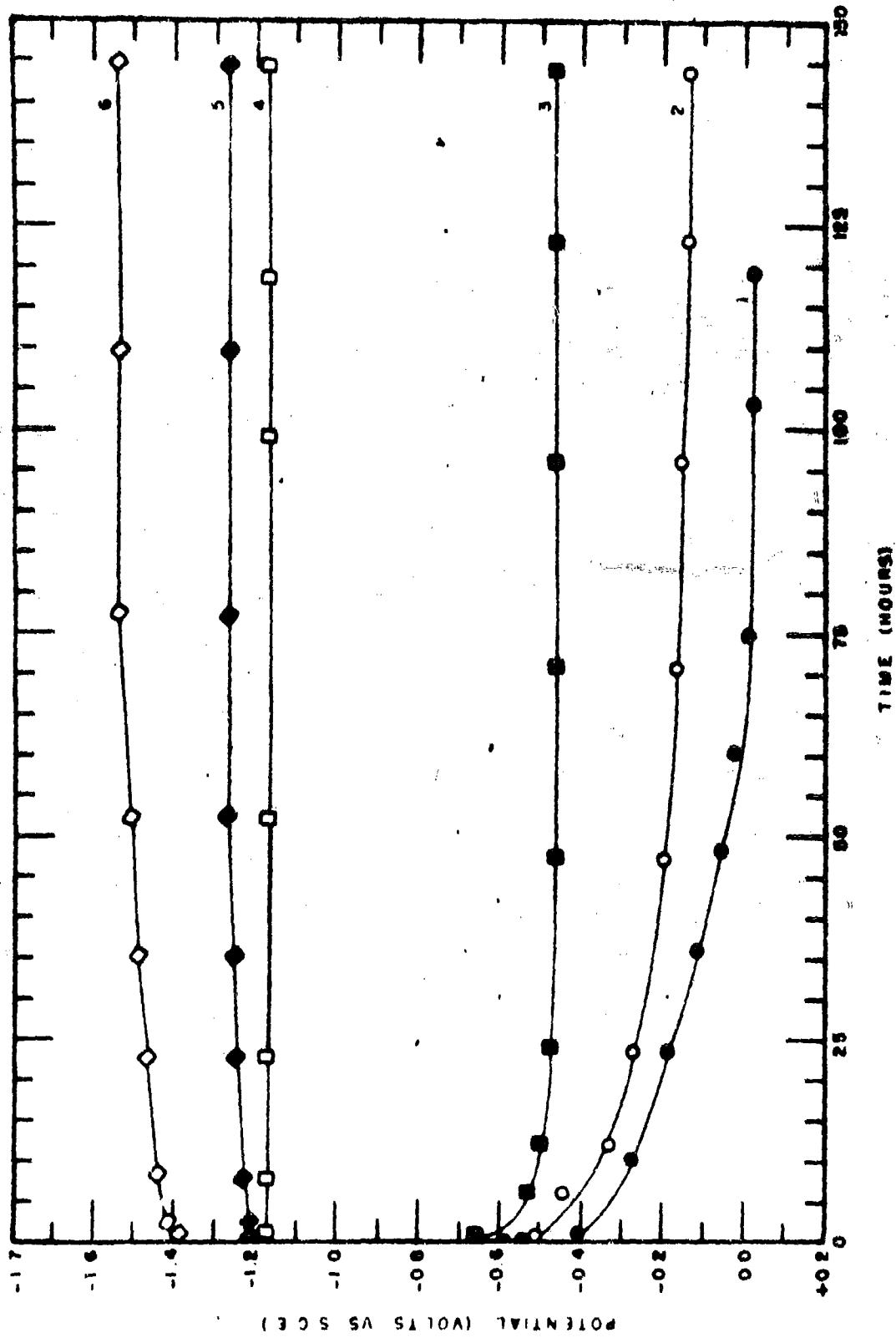
#### Cathodic Time-Potential Studies

Typical time-potential curves at various current densities for cathodically polarized zirconium in 0.5 molar aerated NaCl solutions are shown in Figure 3. Data points marked with the

**FIGURE 3**

**Time-potential curves for cathodic polarization  
of zirconium in aerated 0.5 molar NaCl at 30°C.**

<u>Curve No.</u>	<u>Current density (amp./cm.<sup>2</sup>)</u>
1	0.0
2	$3.5 \times 10^{-8}$
3	$1.8 \times 10^{-5}$
4	$1.8 \times 10^{-4}$
5	$3.5 \times 10^{-4}$
6	$1.8 \times 10^{-3}$



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same figure represent potentials of the same coupon in a continuous run. In this and all following figures, the potential scale is plotted with the negative or anodic potentials at the top. In describing the curves, an increasing potential is moving in the positive direction, or downward on the curve; and a decreasing potential in a negative direction, or upwards.

Curves 1 and 2 are typical for very low current densities, up to  $1 \times 10^{-7}$  amp./cm.<sup>2</sup>. The potentials begin initially at a rather high negative value and increase in a matter of seconds to a potential of about -0.50 volt. The potentials then increase slowly, becoming almost constant in 1 to 3 days. The open circuit potential (curve 1) continues to increase very slowly even after five days.

Curve 3, for  $1.8 \times 10^{-5}$  amp./cm.<sup>2</sup>, is typical for current densities from  $1 \times 10^{-7}$  to  $5 \times 10^{-5}$  amp./cm.<sup>2</sup>. The potential increases rapidly for the first few hours, reaches a steady state within one day, and remains essentially constant thereafter.

Curve 4, for  $1.8 \times 10^{-4}$  amp./cm.<sup>2</sup> and drawn as the average potential reading, is typical for current densities occurring in the region of  $1 \times 10^{-4}$  amp./cm.<sup>2</sup>. The potentials oscillated quite rapidly and an average reading for a period of one minute was recorded as an average potential. These oscillations often were as large as  $\pm 0.2$  volt. In this region, the steady-state potential is reached within one hour and remains constant the remainder of the run.

Curves 5 and 6 are typical for higher current densities,  $3 \times 10^{-4}$  to  $4 \times 10^{-3}$  amp./cm.<sup>2</sup>. The potentials, varying only slightly throughout the entire run, decrease slowly for the first one or two days and then remain constant.

Duplicate runs for the same current densities showed no great dissimilarity in their time-potential curves.

#### Cathodic Polarization Studies

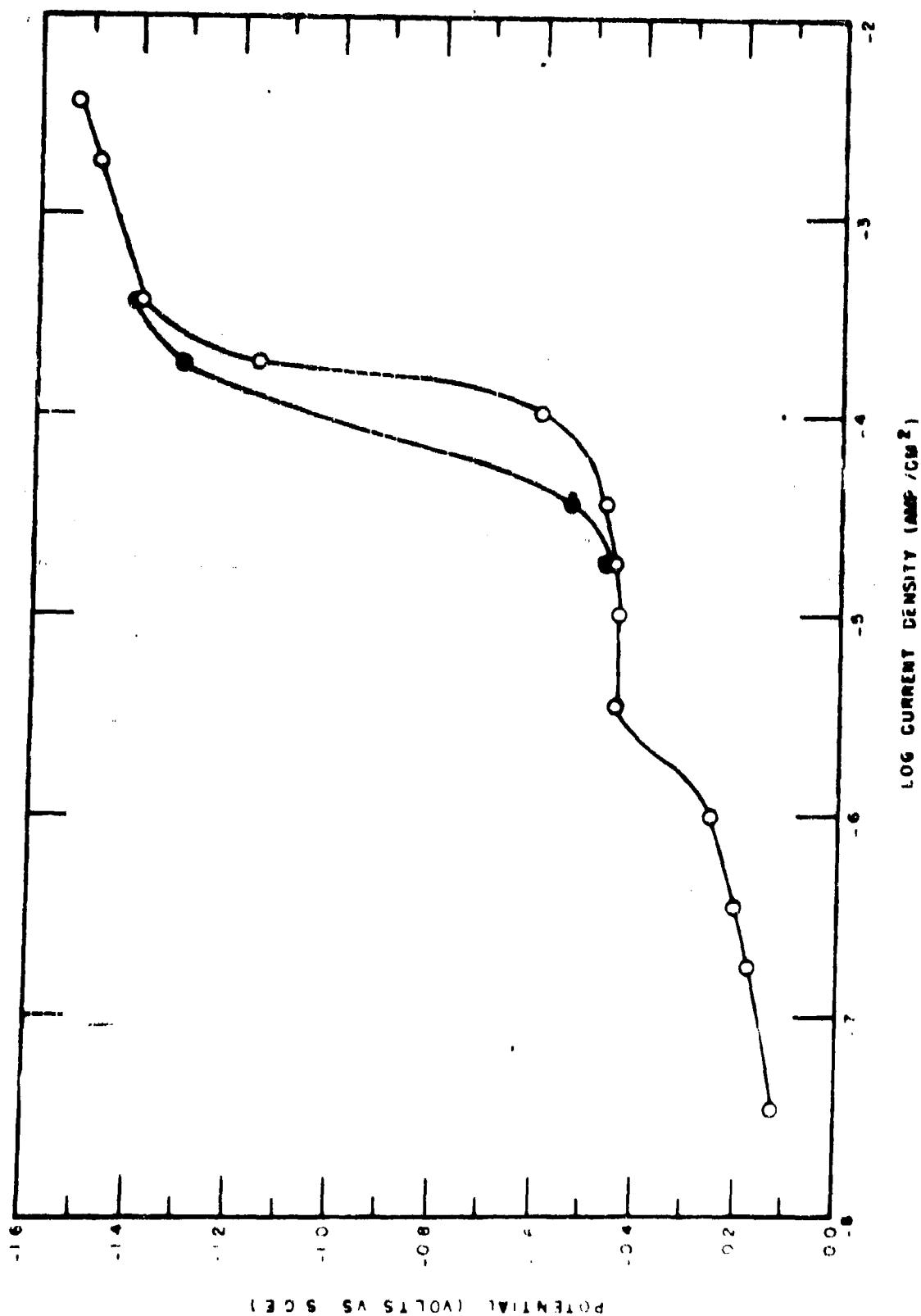
Cathodic polarization curves for zirconium in aerated 0.5 and 1.0 molar NaCl solutions are shown in Figure 4.

All of the points for the 0.5 molar NaCl polarization curve represent constant potentials obtained from coupons held at the original current density for the entire run. Enough points were determined to enable the drawing of all the details of the curve.

**FIGURE 4**

**Cathodic polarization curves for zirconium  
in aerated NaCl solutions at 30°C.**

- 0.5 molar
- 1.0 molar



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Although each point represents a separate run, two or more runs at many of the same current densities were in good agreement. The measurements in 1.0 molar NaCl were made to determine the effect of changing the salt concentration. The points represent constant potentials obtained from one coupon run successively at several current densities. The open circuit potential in 0.5 molar NaCl is 0.013 volts.

Two waves occur in the polarization curve for the 0.5 molar solution; one at a current density near  $2 \times 10^{-6}$  amp./cm.<sup>2</sup>, and the other near  $2 \times 10^{-4}$  amp./cm.<sup>2</sup>. For 1.0 molar NaCl the steep break comes at a lower current density than for the lower concentration. At  $2 \times 10^{-4}$  amp./cm.<sup>2</sup>, gas begins to be evolved slowly on the zirconium. Although visible bubbles do not form on the surface, large bubbles may be observed gathering on the wax coating around the edge of the coupon. At higher current densities, visible bubbles are evolved continuously from the coupon surface. After an extended period of polarization in this region of current density, the zirconium surface is darkened considerably. If the period of polarization is extended to one or two days, the surface becomes coated with a layer of fine black powder. The slope of the straight line obtained in the gas evolution current density range, corresponding to the constant b in the Tafel equation, is 0.15 volt per log unit.

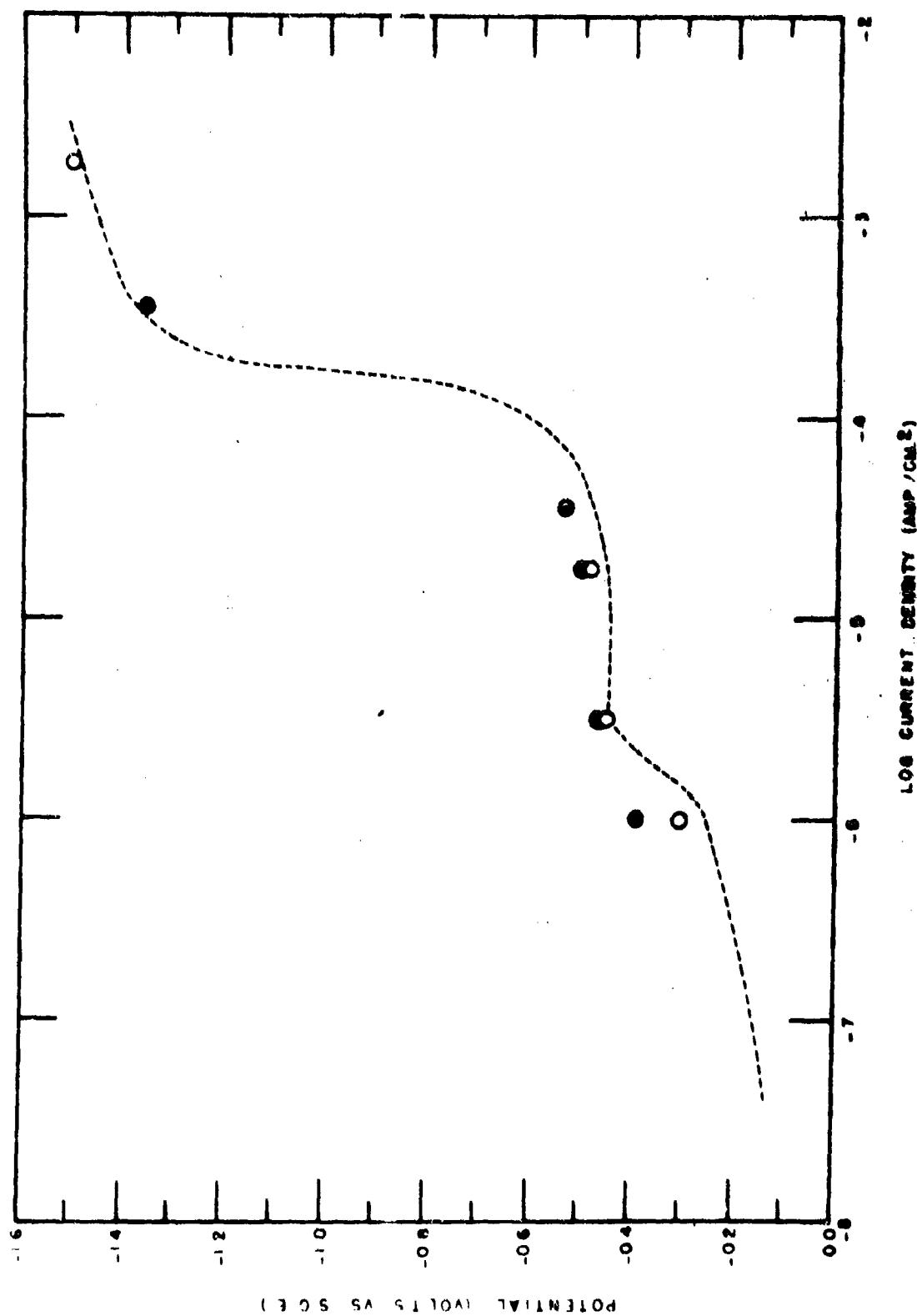
In many instances, it was desirable to determine the effect of various variables, such as salt concentration, by determining only sections of the polarization curve. This could be most readily accomplished by running one coupon at the several current densities. To investigate the validity of potentials obtained in this manner, a complete polarization curve, shown in Figure 5, was obtained from one coupon.

A coupon was started at a current density of  $1 \times 10^{-6}$  amp./cm.<sup>2</sup>, and this was successively increased through other values to  $2 \times 10^{-3}$  amp./cm.<sup>2</sup>. These potentials are represented in the figure by open points. The remaining values, represented by closed points, were determined at decreasing current densities. It can be seen from a comparison with the 0.5 molar curve of Figure 4 that no great dissimilarity between the two curves exists. A small amount of hysteresis is observed in the region of the break occurring near  $2 \times 10^{-6}$  amp./cm.<sup>2</sup>. This is evident in Figure 5 on observing the two potentials for  $1 \times 10^{-6}$  amp./cm.<sup>2</sup>. The reality of this difference was demonstrated by removing the coupon from the solution after a constant potential had been reached, polishing and cleaning in the usual manner, and replacing the coupon in the solution at the same current density.

**FIGURE 5**

Cathodic polarization curves for zirconium  
in aerated NaCl solution at 30°C.

- Increasing current density
- ◐ Decreasing current density
- 0.5 molar curve from Figure 4



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The steady-state potential then reached was the same as the open point in the figure for this current density, the first point obtained in the run.

#### Effect of Surface Pre-treatment on Cathodic Polarization

To determine the effect of surface pre-treatment, one zirconium coupon was polished and cleaned in the usual manner and, just prior to immersion in the salt solution, was cleaned in 5% aqueous hydrofluoric acid, rinsed in 2 N sulfuric acid, and thoroughly rinsed with distilled water. The resulting polarization curve obtained from the coupon in 0.5 molar NaCl is shown in Figure 6.

#### Effect of Oxygen Concentration on Cathodic Polarization

Several preliminary experiments were made to determine the general nature of the effect of oxygen concentration on cathodic polarization of zirconium. These experiments consisted of decreasing the oxygen concentration by cessation of aeration and bubbling nitrogen through the solution, and of increasing the oxygen concentration by aeration with oxygen instead of air. Changing the concentration in this manner resulted in temporarily changing the polarization potentials. These temporary changes appeared interesting enough to warrant further investigation.

To determine if leaching of the plastic containers affected the polarization potentials, several pieces of the same type plastic were immersed in one of the containers used for the aerated runs after the coupon in the container had reached a constant potential. No change in potential was observed after a period of five days.

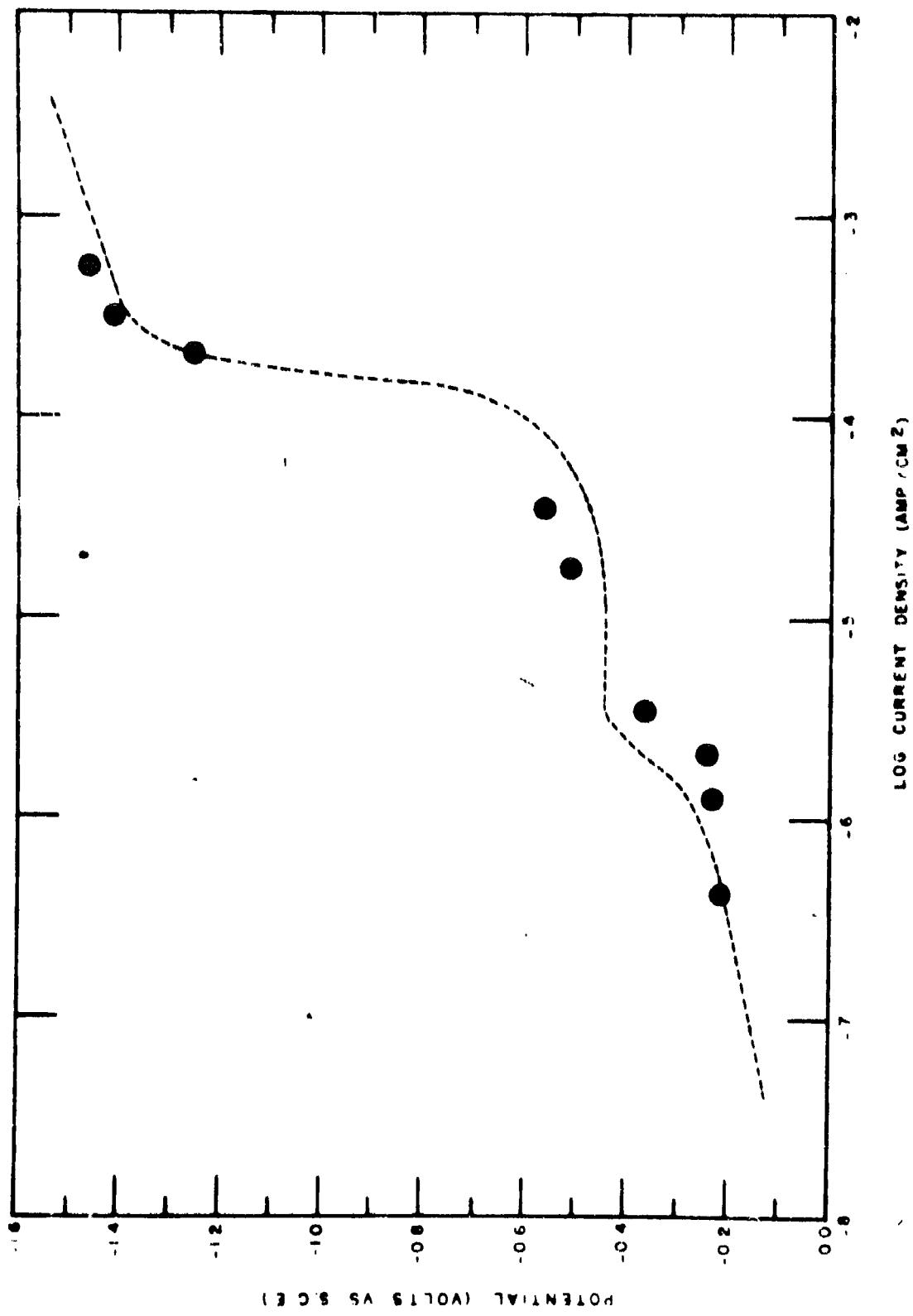
The cathodic polarization curves for zirconium in aerated and air-free 0.5 molar NaCl solutions are given in Figure 7. In this work, it was not necessary to rigorously exclude all oxygen as in hydrogen overvoltage measurements. The curve represented by open circles was obtained first with oxygen excluded as completely as feasible with the apparatus. The portion of the curve represented by the closed triangles was obtained after the completion of the previous determinations by opening the cells to the atmosphere and aeration for a period of only one hour. The curve represented by the closed circles was obtained with the cells open to the atmosphere and undergoing continuous aeration.

The aerated and air-free curves are essentially the same, the difference being in displacement along the current density axis.

**FIGURE 6**

Cathodic polarization curves for zirconium  
in aerated NaCl solution at 30°C.

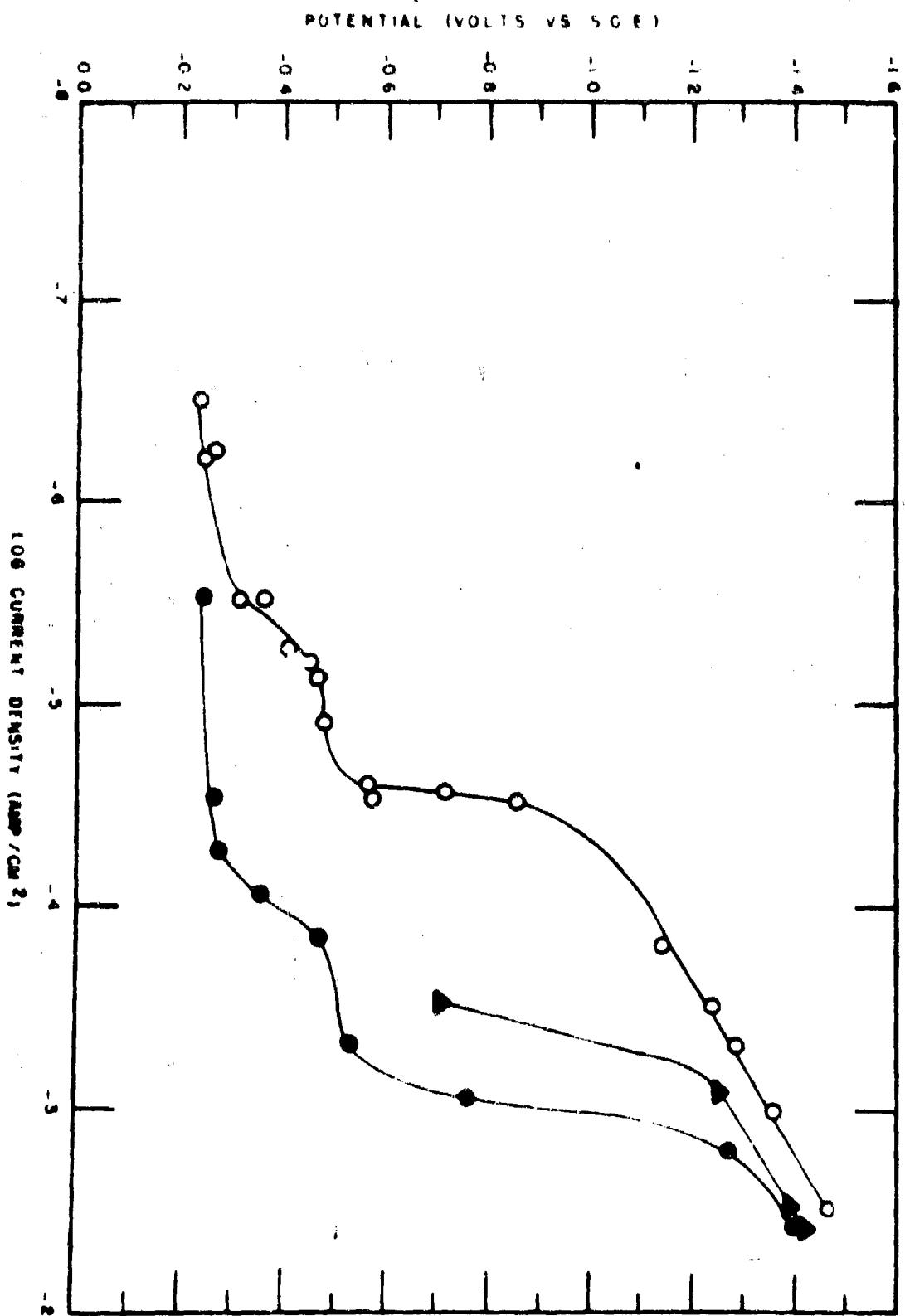
● HF pre-treated coupon  
--- 0.5 molar curve from Figure 4



**FIGURE 7**

Cathodic polarization curves for zirconium  
in 0.5 molar NaCl at room temperature

- Air-free solutions
- ▲ Solutions open to atmosphere
- Aerated solutions



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During the air-free run, it was not possible to determine if any gas was being evolved from the cathode since the cells were completely enclosed, but such evolution was noticed at the higher current densities in the aerated runs. During the runs at high current densities, chlorine gas was detected in the platinum anode chambers.

Because of the difficulty arising from working with a closed system, it was not possible to measure the IR drop of the solution separating the coupon and the saturated calomel reference cell. Consequently, the points shown in Figure 7 have had no correction applied.

#### Anodic Time-Potential Studies

Anodic time-potential curves for zirconium in aerated 0.5 molar NaCl solutions are shown in Figures 8 and 9. In each case after an initial rapid increase from high negative values, the curves increase linearly with time, break sharply, and become horizontal. The increase of potential at higher current densities (Figure 9) was so rapid that no reading could be obtained for at least one minute, and consequently, the initial high negative potentials are not shown in the figure. The curve of Figure 8 for a current density of  $3.5 \times 10^{-8}$  amp./cm.<sup>2</sup> differs from the others by having a slight curvature in the early portion of the curve. It is to be noted that the horizontal portions of the curves all lie at approximately the same potential.

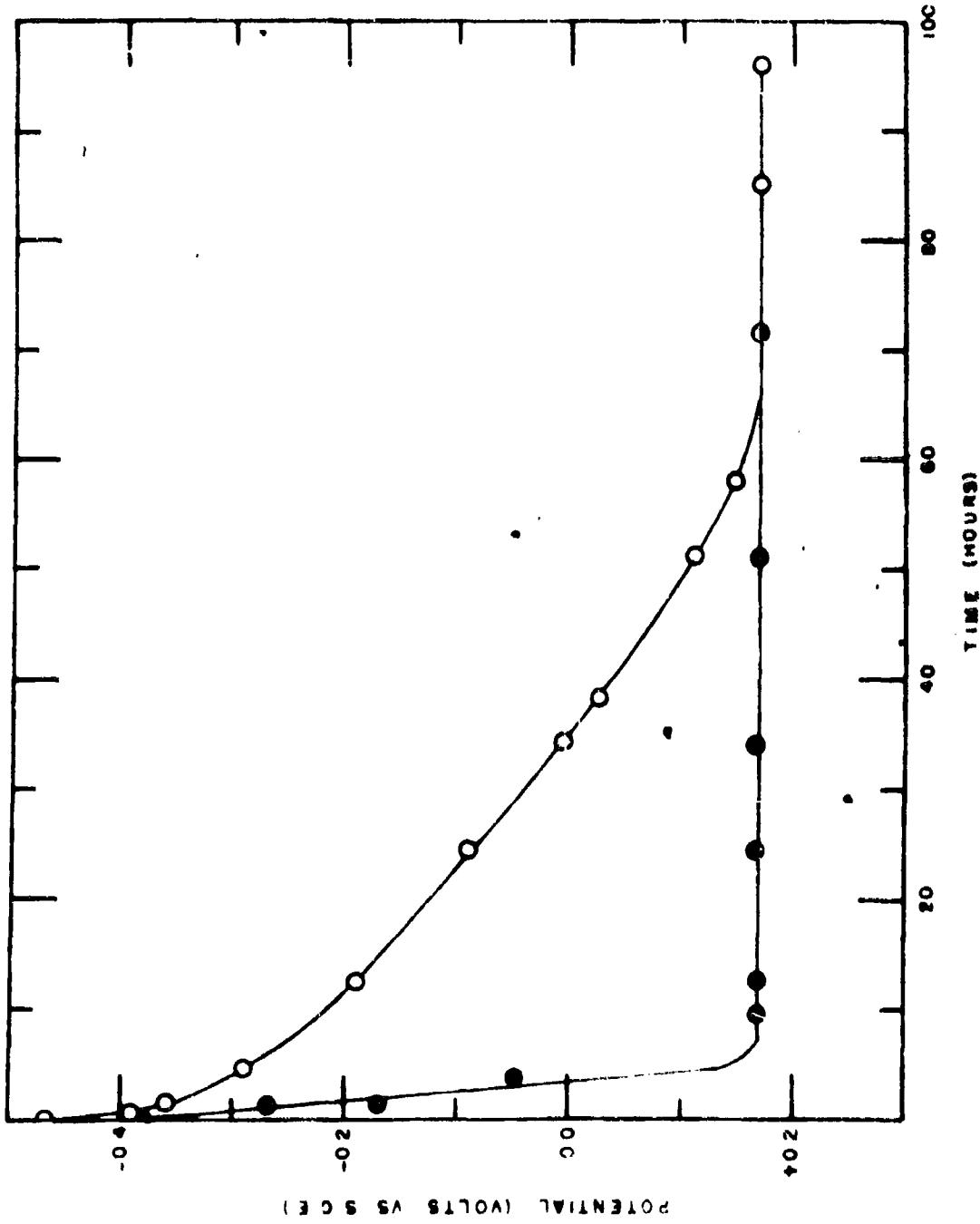
A time-potential curve for zirconium in aerated 0.5 molar Na<sub>2</sub>SO<sub>4</sub> at a high current density,  $1.8 \times 10^{-3}$  amp./cm.<sup>2</sup>, is shown in Figure 10. The potential rapidly increased from an initial negative value, apparently leveled off somewhat in about 10 minutes time at a potential of about 1.7 volts. Within a total time elapse of 15 minutes, however, the potential began a second rapid increase. During the time of this increase, the potential changed so rapidly that no measurement could be made. When it was finally possible to obtain a reading, the potential, oscillating quite rapidly within a range of  $\pm 1.0$  volt, leveled off at an average value of 28.5 volts. The potential remained at this value for an hour, at which time the current density was decreased to  $7 \times 10^{-4}$  amp./cm.<sup>2</sup>. Almost immediately the potential decreased to 14.5 volts where it remained until the end of the run. At this potential also the oscillations were quite large and an average reading was necessary.

During the initial few minutes of the run when the potential had apparently leveled off, gas evolution from the surface of the zirconium could be seen. However, when the sudden increase in potential occurred, gas evolution ceased. When the coupon

**FIGURE 8**

Time-potential curves for anodic polarization of  
zirconium in aerated 0.5 molar NaCl at 30°C.

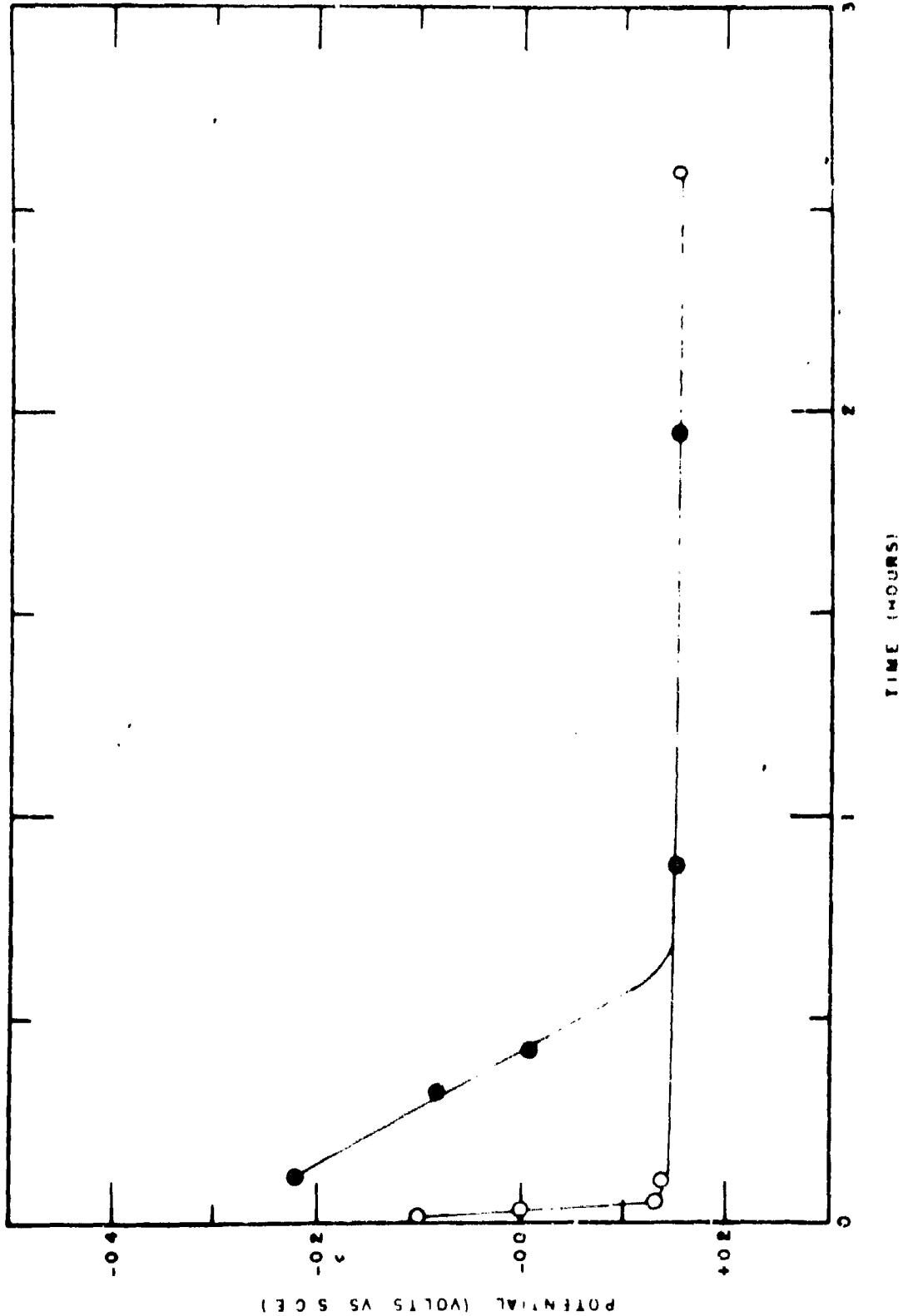
- $3.5 \times 10^{-8}$  amp./cm.<sup>2</sup>
- $3.5 \times 10^{-7}$  amp./cm.<sup>2</sup>



**FIGURE 9**

Time-potential curves for anodic polarization of  
zirconium in aerated 0.5 molar NaCl at 30°C.

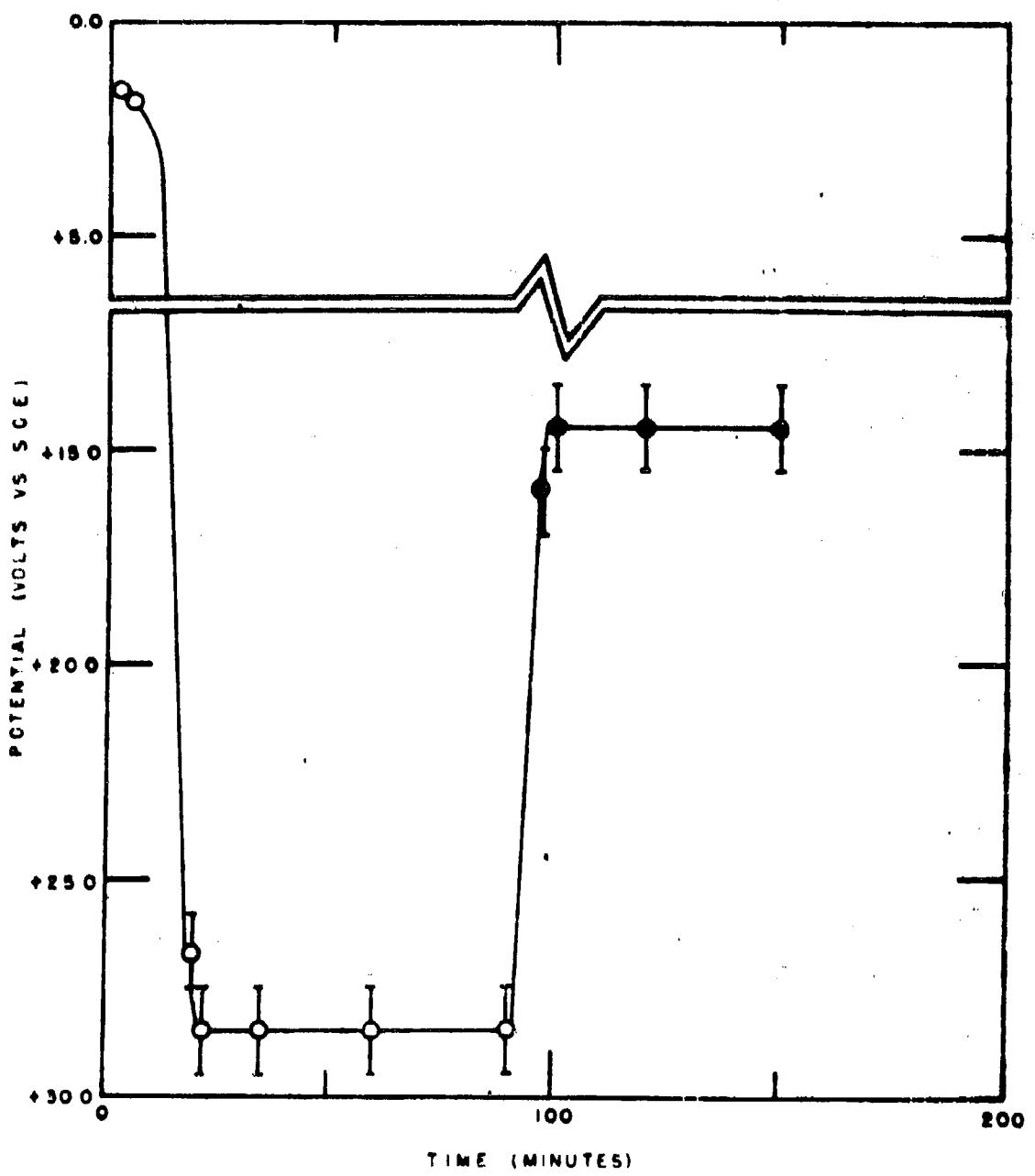
- $3.5 \times 10^{-6}$  amp./cm.<sup>2</sup>
- $1.8 \times 10^{-5}$  amp./cm.<sup>2</sup>



**FIGURE 10**

**Time potential curve for anodic polarization of  
zirconium in aerated 0.5 molar  $\text{Na}_2\text{SO}_4$  at 30°C.**

- $1.8 \times 10^{-3}$  amp./cm.<sup>2</sup>
- $7.0 \times 10^{-4}$  amp./cm.<sup>2</sup>



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used in this study was removed from the salt solution, the surface was darkened considerably. The entire surface was slightly etched with a few deep pits in evidence around the edge of the coupon.

#### Anodic Polarization Studies

The anodic polarization curve for zirconium in aerated 0.5 molar NaCl solution is shown in Figure 11, Curve 2. The most important observation from the curve is the fact that the potential is independent of the current density. At the lowest current density,  $3.5 \times 10^{-7}$  amp./cm.<sup>2</sup>, the surface of the coupon, on removal from the solution after the completion of the run, was slightly duller in color than the freshly polished one. Coupons run at progressively higher current densities exhibited increasing amounts of surface attack. One coupon, run anodically at a current density of  $3.5 \times 10^{-2}$  amp./cm.<sup>2</sup> for less than 36 hours, dissolved almost completely. During the course of the run, a large amount of a white gelatinous precipitate collected on the bottom of the polarization cell. When washed and dried, this precipitate turned a dark blue. The front surface of the remaining portion of the coupon was black and flaky; whereas the back was essentially unchanged and showed no signs of attack.

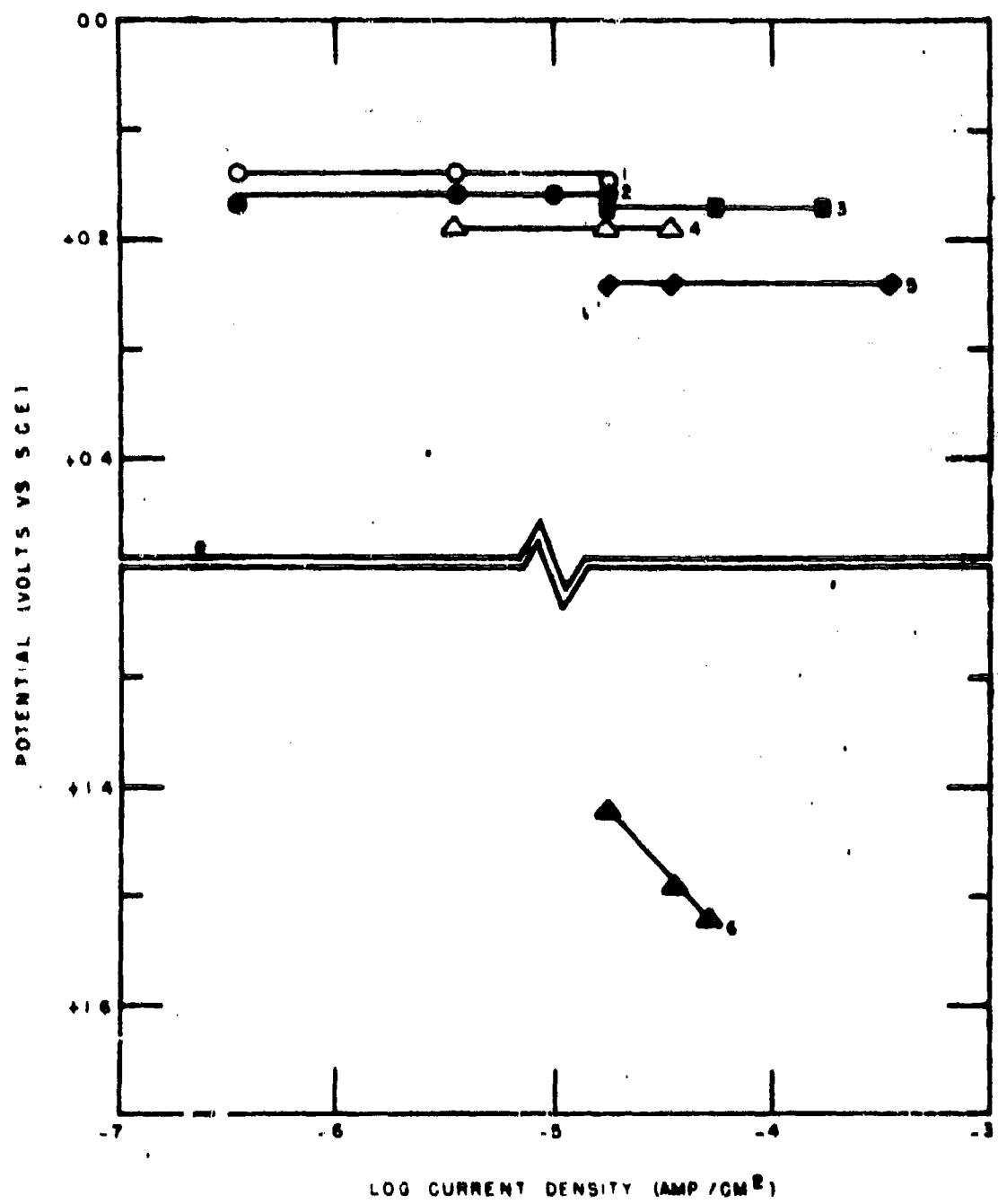
An electron diffraction pattern of the coupon surface was made. The surface was extremely fragile, therefore, it was not possible to wash it and lines corresponding to the spacings of NaCl were quite predominant in the diffraction pattern. The lines present, other than those belonging to NaCl, could not be indexed as belonging to any known compound of zirconium whose spacings have been reported. An x-ray diffraction pattern was made of a sample of the dried precipitate collected from the bottom of the polarization cell. Again, the lines could not be indexed as belonging to any reported compound of zirconium; however, if the sample were considered a mixture rather than a pure compound, over half of the lines present in the diffraction pattern could be accounted for.

During one of the anodic runs in aerated 0.5 molar NaCl solutions, chlorine gas was bubbled directly over one coupon. Although no change in potential was observed, a comparison of the coupon surface with one from an earlier determination at the same current density showed that the degree of attack was considerably increased by the presence of the chlorine.

FIGURE 11

Anodic polarization curves in  
unstirred solutions at 30°C.

<u>Curve No.</u>	<u>Metal</u>	<u>Solution</u>
1	Zr	0.7M NaCl
2	Zr	0.5M NaCl
3	Zr-Hf	0.5M NaCl
4	Zr	0.2M NaCl
5	Hf	0.5M NaCl
6	Zr	0.5M Na <sub>2</sub> SO <sub>4</sub>



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#### Effect of NaCl Concentration on Anodic Polarization

The effect of NaCl concentration on the anodic polarization of zirconium was investigated by determining polarization curves in 0.7 and 0.2 molar NaCl solutions in addition to the studies in the 0.5 molar solutions just discussed. The results are shown in Figure 11, Curves 1 and 4 respectively. The curves, again independent of current density, show potentials slightly less positive for the 0.7 molar salt and slightly more positive for the 0.2 molar solution than were obtained in the case of the 0.5 molar solutions. The coupons used in these runs showed signs of attack similar to those previously observed; the degree was dependent on the current density.

Cessation of aeration during the runs carried out in NaCl solutions resulted in no change in electrode potentials.

#### Effect of Hafnium on Anodic Polarization

A study on the effect of hafnium on the anodic polarization studies was carried out to determine if either the presence or absence of the metal was an important factor in the anodic dissolution of zirconium in NaCl solutions. Anodic polarization curves were determined with commercial zirconium and with zirconium-free, hafnium coupons. The results, given in Figure 11, Curves 3 and 5 respectively, show little deviation from those obtained with hafnium-free, zirconium. The constant potential obtained with commercial zirconium is essentially the same as that for the pure metal; however, a definite difference in potential is obtained with the pure hafnium coupon. In all cases there is evidence of attack of the surface of the metal in question.

#### Effect of Electrolyte on Anodic Polarization

Curve 6 of Figure 11 gives the results of an anodic polarization study of zirconium in aerated 0.5 molar  $\text{Na}_2\text{SO}_4$  solution. Only a portion of the complete polarization curve was determined since the results of the few points obtained clearly demonstrated that the metal was passive in the sulfate solution. At the three current densities reported, a gas, presumably oxygen, was evolved at the zirconium anode. After four days, the coupon was removed from the solution just long enough to observe the surface. No change in the appearance of the coupon was evident. When the coupon was returned to the electrolyte solution, the potential immediately went to the constant value the coupon possessed before being removed from the solution.

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A sufficient quantity of NaCl was added to the sulfate solution to make the solution approximately 0.5 molar with respect to chloride. The electrode potential decreased rapidly from 1.5 volts to 0.18 volts. The latter potential is only slightly different from that obtained with the 0.5 molar NaCl solution alone.

### Discussion

#### Cathodic Polarization

The usual cathodic reactions in aerated aqueous solutions containing no foreign reducible materials are the reduction of dissolved O<sub>2</sub> to OH<sup>-</sup> and the reduction of H<sub>4</sub> to H<sub>2</sub>. The complexity of the former is not completely known; however it occurs at a less negative potential than the latter and thus precedes hydrogen evolution as the current density is increased. The results of this study show that a zirconium cathode in neutral chloride solutions follows this pattern. Thus, up to a current density of about  $2 \times 10^{-4}$  amp./cm.<sup>2</sup> (see Figure 4) the electrode reaction is presumably the reduction of O<sub>2</sub>. The step in the curve occurring at a current density near  $2 \times 10^{-6}$  amp./cm.<sup>2</sup> will be discussed later. The step occurring at  $2 \times 10^{-4}$  amp./cm.<sup>2</sup> represents the limiting diffusion current, or current density, for oxygen under the experimental conditions. At current densities above this value, hydrogen is evolved. The air-free investigations were carried out in order to check the validity of the assumption that the break was the diffusion wave representing the limiting diffusion current of oxygen.

Since the geometry of the electrode assembly used in the air-free studies was quite different from that used in the aerated studies, it was considered inadvisable to attempt a correlation between runs in the different pieces of apparatus. In order to eliminate this obstacle, both aerated and air-free runs were made in the apparatus constructed for air-free studies. The curves shown in Figure 6 demonstrate that the reduction in oxygen concentration lowered the limiting diffusion current.

Apparently, the only effect of changing the chloride concentration was to change the limiting diffusion current of O<sub>2</sub>. Since the limiting diffusion current of a substance is proportional to its concentration, it would be expected that this current would be proportional to the solubility of oxygen in the two different concentrations of the salt solutions used. From data for oxygen solubilities in sodium chloride solutions (7), the expected ratio of the diffusion currents in 1.0 and 0.5 molar solutions,

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$I_d \text{ 1.0M}/I_d \text{ 0.5M}$ , can be calculated. The calculated ratio, 0.86, compares reasonably well with the observed ratio, 0.7. If the details of the 1.0 molar curve in the region of the break were better known, the comparison would probably have been even better.

From the ratios of the limiting diffusion currents for the studies involving oxygen concentration, the concentration of dissolved oxygen in the air-free determination is calculated to have been  $3.1 \times 10^{-6}$  molar, corresponding to an oxygen partial pressure of 2.5 mm. In a similar manner, the oxygen partial pressure in the partially aerated run was calculated to have been 57 mm.

At current densities larger than the oxygen limiting diffusion current hydrogen is evolved and the potentials follow a Tafel relationship for hydrogen overvoltage. In the aerated systems the potential of the electrode is given by the equation

$$E = -1.47 - 0.15 \log i$$

where  $i$  is the current density in milliamp./cm.<sup>2</sup>.

Oxervoltage,  $\eta$ , is defined as the difference between the measured and the reversible electrode potentials and is always given a positive value. The pH of the solution was 6.5, therefore the reversible hydrogen potential on the saturated calomel cell is -0.63 volt. The hydrogen overvoltage on zirconium is then given by the equation

$$\eta = 0.84 + 0.15 \log i.$$

At  $1 \times 10^{-3}$  amp./cm.<sup>2</sup>, the overvoltage is 0.84 volt. Values for the constant  $b$  in the Tafel equation usually fall between 0.09 and 0.13. However, the value obtained for zirconium, 0.15, is not unique since high values have been reported for such metals as titanium, mercury, and lead among others.

The hydrogen evolution portion of Figure 7 can be corrected for the solution IR drop if it is assumed that the solution resistance for the aerated and air-free determinations are the same. Any error because of this assumption would probably be negligible compared to the accuracy of the data. The slope of the corrected curve, not shown in Figure 7, is 0.16 while the overvoltage at 1 milliamp./cm.<sup>2</sup>,  $\eta$  1 ma./cm.<sup>2</sup>, is 0.72 volt.

Hydrogen overvoltage depends on the current actually involved in

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hydrogen evolution rather than on total current. Consequently, it would be better to represent the hydrogen overvoltage as the relationship between  $E$  and  $\log (I - I_d)$ , i.e., total current minus the oxygen limiting diffusion current. Such a relationship results in a line having a slightly less positive slope. For the aerated run, the slope and the overvoltage at 1 milliamp./cm.<sup>2</sup> are 0.12 and 0.83 volt respectively. Similar values for the air-free determination are 0.15 and 0.71 volt for the slope and the overvoltage at 1 milliamp./cm.<sup>2</sup> respectively.

A comparison of the overvoltage values for the aerated and air-free runs is not good. Perhaps the large difference in geometry of the two systems can account to some extent for the difference. The air-free electrode assembly construction allowed only an average reading of the potential of the coupon; while very likely the polarizing current was blocked from the surface of the metal coupon for a large portion of the time. Blocking the polarizing current from a portion of the coupon surface results in a lower observed potential. Thus, if a large amount of current was blocked from the coupon surface, the observed potential would definitely be too low. A correction would tend to raise the observed overpotential for the air-free determination. In what manner the potential error would change with current density and thus effect the slope of the curve in the hydrogen evolution region is not known. From these observations, it appears that the more nearly correct overvoltage values are those obtained from the aerated studies. Although the comments above seemingly make the air-free data unusable for overvoltage calculations, they do not detract from the validity of the determinations for the oxygen diffusion current relationships.

As mentioned earlier, after hydrogen evolution for extended periods of time, the surface of the zirconium coupon became black and hard. If the periods of evolution were very long and the evolution was rapid, the surface became covered with a thin layer of black powder. Apparently in this region, either a hydride or a solid solution of the metal with hydrogen is produced. Both have been reported from zirconium (8, 9). The presence of a hydride produced by cathodic treatment of zirconium has been previously reported in the literature (10).

The current density region below the oxygen limiting diffusion wave has been previously attributed to the cathodic reduction of  $O_2$  to  $OH^-$ . If the polarization curve were drawn as the best straight line from the lowest current density studied to the break occurring at  $2 \times 10^{-4}$  amp./cm.<sup>2</sup>, the slope of the line would be

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nearly the same as the constant b in the Tafel equation found for the hydrogen evolution portion of the curve. This would indicate that the reduction of  $O_2$  to  $OH^-$  followed an overvoltage equation similar to that for hydrogen. However, the step occurring at  $2 \times 10^{-6}$  amp./cm.<sup>2</sup> is definitely present under the existing experimental conditions. Several possible explanations for such a break present themselves:

- (i) Changing from the two-electron reduction of  $O_2$  to  $H_2O_2$  to the four-electron reaction for the reduction to  $OH^-$ .
- (ii) Reduction of some impurity in the solution.
- (iii) Production of a depolarizer by electrolysis.
- (iv) Reduction of some metallic component of the system, say a surface oxide.

The experimental evidence for the break indicates that it is oxygen dependent analogous to the break occurring at a current density of  $2 \times 10^{-4}$  amp./cm.<sup>2</sup>. This would indicate that the explanation is one involving a step in the reduction of  $O_2$  to  $OH^-$  as in (i). However, the two breaks occur at current densities differing by a factor of 100. Such a difference would mean that if the break occurring at the higher current density were for the four-electron reduction, the lower break must be for a process involving a fractional electron change. Thus this explanation is hardly acceptable. For the two breaks to be an indication of a stepwise reduction would involve a mechanism probably very complex. It is not clear in what manner such a reduction would operate.

Explanation (ii) is hardly likely since the solutions were pre-electrolyzed with no resulting change in the curve.

If the wave represented the limiting diffusion of some depolarizer formed by electrolysis, the time potential curves for low current density values (Figure 3, Curves 1, 2, and 3) would have increased sooner the higher the current density since the concentration of the depolarizer being formed would increase more rapidly at these higher current densities. Instead, the reverse is observed. This would seem to eliminate possibilities (i) and (iii).

Thermodynamically, a surface film of  $ZrO_2$  or other such oxide could exist at the potentials observed. The existence of such a film at low cathodic current densities has been postulated (10). It is not believed that such an oxide film would withstand the

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cathodic reduction at higher current densities, especially in the hydrogen evolution portion. Although etching in hydrofluoric acid would probably strip such an oxide film from the metal, when the metal was exposed to a solution saturated with oxygen, the film could re-form.

If the reduction of such a surface film is the explanation of the break in the polarization curve occurring at the lower current density, the mechanism of the film formation must involve a direct oxidation of the surface by the dissolved oxygen to explain the data. This is in contrast with Warner's work (10) which merely postulated the reaction of the metal with water to form the oxide.

The hysteresis observed in the region is best explained as the result of a surface change of the metal caused by hydrogen evolution.

The cathodic polarization curve for zirconium (Figure 4) is probably typical for zirconium in other aerated salt solutions, unless a specific reaction occurs and, thus, any change in type of salt or salt concentration should result only in effects resulting from pH changes or oxygen solubility changes. The general shape of the curve should be typical for other non-corroding metals in similar solutions.

#### Anodic Polarization

When zirconium is treated anodically in neutral sodium chloride solutions, the metal dissolves. No definite indication of weight loss would be detected at the lower current densities studied, about  $1 \times 10^{-6}$  amp./cm.<sup>2</sup>, since the total amount of electricity passed would cause a weight loss of less than 1 mg. of metal. At the higher current densities metal loss was quite evident since one coupon dissolved almost completely in less than 36 hours.

No real difference is observed between pure zirconium, commercial zirconium, and hafnium on anodic treatment in neutral chloride solutions. All dissolve at a characteristic potential which remains constant with a change in current density. It is evident that hafnium would be expected to dissolve at a potential somewhat different from that of zirconium. Since the potential for hafnium dissolution is more positive than for zirconium, commercial zirconium would be expected to dissolve at essentially the same potential as the pure metal.

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Under similar anodic treatment in neutral sodium chloride solutions, titanium was observed to be passive (5). Because of the similarity between the metals, one would predict that any mechanism for the dissolution of zirconium in chloride solutions would apply equally well to titanium. Conversely, any mechanism for the passivity of titanium in chloride solutions should apply as well to zirconium. No explanation for this anomaly can be given.

A similar treatment of the metal in neutral sulfate solution resulted in passivation of the metal with accompanying oxygen evolution from the electrode. If sodium chloride is added to the sulfate solution, the metal again becomes active as indicated by the observed sudden decrease in potential. When such a decrease occurred, the metal again dissolved.

The passivity of zirconium in sulfate solutions may be explained by the formation of a protective layer of an insoluble, or only sparingly soluble, oxide film on the surface of the metal. At higher current densities this layer may grow until it becomes visible. The presence of reducing agents or cathodic treatment destroys this oxide layer, resulting in loss of passivity.

Since chlorine gas bubbled over the zirconium coupon had no effect on the electrode potentials, no mechanism dependent on the presence of  $\text{Cl}_2$  would be applicable. This eliminates discharge of  $\text{Cl}^-$  to  $\text{Cl}_2$  at the anode. The mechanism of the dissolution involves a transfer of metal, in the form of a zirconium or zirconyl ion, across the metal-solution interface. This ion then combines with  $\text{Cl}^-$  to form a soluble salt. As more positive metal ions are transferred, more salt is formed. The salt should hydrolyze readily at the solution pH to form the dioxide of the metal, probably in the hydrated form which is stable.

The action of a zirconium anode as an electrolytic rectifier has been known for some time. More recently, this electrolytic action has been compared with that for tantalum (11). The valve action of both metals is dependent on a surface film of oxide which allows current to flow cathodically, but blocks current flow anodically. The action of the film is postulated as a potential barrier effect and not merely an IR effect. The essentials for a postulated mechanism for rectification of tantalum have been given by Haring (12). In this mechanism, if a voltage lower than the film forming voltage is applied anodically, the anode acts as a rectifier and blocks current flow. If a voltage higher than the initial film forming voltage is applied anodically, the film thickens. This is applicable up to the breakdown voltage

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of about 100 volts, or unless the film is broken down by a discharge of some ion which furnishes electrons. The electrons in turn move into the solid oxide film, neutralize some of the positive metal ions, thereby decreasing the positive space charge caused by the metal ions permitting the movement of additional positive ions from the metal into the film. These ions tend to follow the path of best conductance established by the inward moving electrons. The result is a sporadic pattern of film growth, and local breakdown of the film would be expected to occur at the areas of highest current density, i. e., at the edges of the coupons. This is the area where the most severe pitting of the zirconium coupons occurred.

The behavior of zirconium in sulfate is probably due to a film formation which reaches a limiting thickness for the applied voltage. When this thickness is reached, the potential levels off slightly and oxygen is evolved from the electrode. The evolution causes a film breakdown according to the mechanism postulated by Haring. The oxygen evolution observed at the low current densities is not rapid enough to furnish electrons fast enough to break down the film. Warner's work in sulfuric acid solutions shows that the duration of this small plateau is inversely related to the anodic current density.

The large positive potentials observed when zirconium was run at high anodic current densities in 0.5 molar  $\text{Na}_2\text{SO}_4$  solutions (see Figure 10) can best be explained as an IR drop across a surface oxide layer acting as an ohmic resistance. Thus, as the current is decreased the potential should decrease proportionally. The observed potential values would correspond to an ohmic resistance of  $5.7 \times 10^3$  ohms for the higher value of current and  $7.2 \times 10^3$  ohms for the lower value. These values are in fair agreement, considering the wide range of voltage oscillations observed.

Further investigation is needed before a more complete explanation of the rectifying action can be formulated. A comparison of the anodic polarization of zirconium at low current densities,  $1 \times 10^{-5}$  amp./cm.<sup>2</sup>, with a similar treatment of a metal which definitely has a rectifying layer on it, would be very advantageous for this purpose.

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